



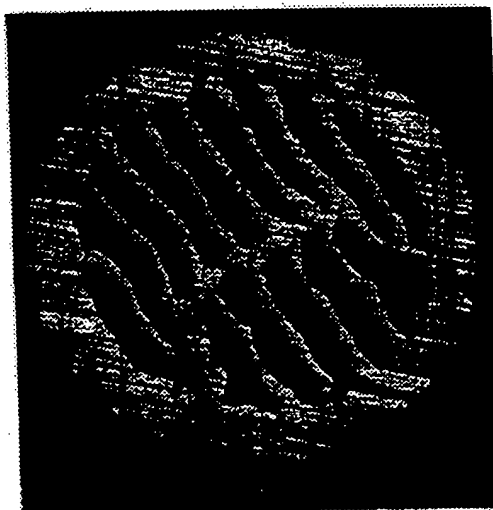
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(54) Title: SUPERCONDUCTING WIRES AND THEIR MANUFACTURE

## (57) Abstract

An axially extending superconducting wire includes a substantially axially extending superconducting filament which is flattened in cross section. The superconducting filament is twisted along at least a substantial portion of its length into a substantially helical shape, such that the wire behaves substantially anisotropically in relation to the effect of an applied magnetic field on the critical current  $I_c$  at any cross-sectional point along the wire's length, and substantially isotropic in relation to the effect of an applied magnetic field on the self-induced critical current  $I_c$  along a substantial length of the wire.



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**TITLE: SUPERCONDUCTING WIRES AND THEIR MANUFACTURE****FIELD OF THE INVENTION**

The present invention relates to ceramic superconductors and the manufacture thereof. In particular, the invention relates to the manufacture of ceramic high temperature superconductors for use in applications requiring superconducting wire which exhibits isotropic behaviour with respect to magnetic fields.

**BACKGROUND OF THE INVENTION**

One of the most promising high temperature superconducting (HTS) materials for power engineering applications at 77K is  $(\text{Bi}_{2-x}\text{Pb}_x)\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-y}$  (BSCCO-2223) processed in a silver sheath via the powder-in-tube (PIT) technique. As it is competing for the most part with copper at approximately 293K, the economic viability of powder-in-tube HTS conductors in electrical engineering depends on the ability to manufacture long lengths of relatively cheap tape or wire, with a 77K, self-field critical current density,  $J_c$ ,  $\geq 2 \times 10^8 \text{ Am}^{-2}$  and a 77K, self-field critical current,  $I_c$ , greater than 30A.

At present, short ( $\approx 50\text{mm}$ ) intermediately-pressed, PIT tapes have shown 77K, self-fields of  $J_c = 7 \times 10^8 \text{ Am}^{-2}$  on selected areas, whilst longer length (10-1000m) powder-in-tube tapes manufactured using conventional or shear/high pressure rolling have shown 77K, self-field  $J_c$  values of  $3 \pm 1 \times 10^8 \text{ Am}^{-2}$ . These  $J_c$  values show that powder-in-tube tapes are just entering the zone where they may be considered as economic competitors to conventional copper-based high power devices.

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The PIT technique is essentially a deformation process whereby a tube, typically silver or a silver alloy, is packed with the powdered ceramic superconductor or a precursor thereof, and repeatedly drawn and/or rolled whereby the ceramic powder is compacted in a sheath. The compacted powder is subsequently sintered. This process may typically be used to produce a metal/superconductor composite wire or tape which consists of one or more continuous superconducting filaments embedded in a metal matrix. It is desirable that the metal provide mechanical support to the ceramic superconductor material, has good thermal conductivity to provide cryostability (maintenance of an even temperature throughout the ceramic superconductor material) and is capable of serving as an electrical conductor in the event that the ceramic superconductor material reverts to the state in which it has normal conductivity, i.e. is no longer superconducting.

In one example of the PIT technique, a multifilament tape may be manufactured by packing a precursor of partially reacted oxides into a sealed silver tube or billet which is then reduced to around 1mm diameter by drawing through dies. The wire is then be passed through a rolling mill to produce a tape. The drawing and rolling processes is typically repeated several times, with intermediate annealing of the silver sheath and heat treatment/sintering of the ceramic, resulting in high temperature superconductor tape typically 3 to 4mm wide and 0.2 to 0.5mm thick. A multifilament tape is produced by stacking a bundle of drawn tapes or wires into another tube, drawing it down to 1~2mm diameter and rolling and heat treating as before. It is preferred to

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use BSCCO-2223 high temperature superconductors since high critical current density,  $J_c$ , is typically obtained with a microstructure of well-aligned superconducting grains with clean grain boundaries and strong flux pinning.

Achievement of acceptable critical current and other parameters has  
5 been found to require superconductors in flat tape form, most preferably having a cross-sectional height to width aspect ratio of approximately 1:10. These tapes are grossly anisotropic and react to magnetic fields in a very anisotropic way: a field applied parallel to the tape may degrade  $J_c$  by 10% but an equal field applied perpendicular to it may degrade it by 50%. In some  
10 applications, an anisotropic superconductor can become twisted along its length in an unpredictable manner, resulting in a  $J_c$  that varies along the length of the superconductor. In many situations, this is undesirable. However, in some cases it is desirable that a superconducting wire behaves substantially isotropically along its length. A conventional approach of  
15 achieving this is to make a roundish assembly with anisotropic tapes disposed in different orientations to achieve overall symmetry.

A physically or geometrically isotropic or symmetrical wire is a wire of at least substantially round cross-section in which all points within the wire and along the wire axis may be mapped onto each other according to the rule  
20  $(R, \phi) \longleftrightarrow (R, -\phi)$  for any arbitrary value of  $\phi$ , where  $R$  is the radial distance from the wire.

Magnetic isotropy at any cross-section along a wire may be satisfied

if:

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$$I_c(R, \phi) = I_c(R, \phi - \alpha), \text{ where } \alpha \text{ is an arbitrary angular offset.} \quad (\text{Eqn 1})$$

Rotational symmetry exists in a wire which has both physical and magnetic isotropy.

European Patent Application EP 0798749, describes the manufacture of a wire with a circular or polygonal cross-section having a high degree of rotational symmetry. The manufacture of such wires involves sophisticated and complex manufacturing processes to achieve the high degree of rotational symmetry, rendering them too expensive to compete with copper conductors.

Unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

#### DISCLOSURE OF THE INVENTION

According to a first aspect of the present invention there is provided an axially extending wire including a substantially axially extending superconducting filament which is flattened in cross section, the superconducting filament being twisted along at least a substantial portion of its length into a substantially helical shape, such that the wire is:

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substantially anisotropic in relation to the effect of an applied magnetic field on the critical current,  $I_c$ , at any cross-sectional point along the wire's length; and

substantially isotropic in relation to the effect of an applied magnetic field on the critical current,  $I_c$ , along a substantial length of the wire.

Preferably, the filament is rotationally asymmetrical about the axis at each point along the length of the wire.

Preferably, the anisotropic and isotropic conditions are satisfied in relation to a magnetic field applied in a plane substantially normal to the axis.

10 Preferably, the wire includes a plurality of the filaments arranged, in cross section, in at least two parallel stacks.

Preferably, each stack contains a plurality of the filaments.

Preferably also, the filaments are embedded in a silver or silver alloy matrix.

15 Preferably, a pitch of the helical shape is selected on the basis of an application to which the wire is to be applied.

Preferably, the pitch of the helical shape is selected on the basis of an expected minimum radius of curvature which the application to which the wire is to be applied.

20 Preferably, the filaments include Pb stabilised BSCCO-2223 ceramic.

According to a second aspect of the invention, there is provided a method of fabricating a superconducting wire, the method including the steps of:

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- providing a primary metallic tube;
- packing precursors of ceramic high temperature superconducting material into the primary metallic tube;
- applying heat to degas the contents of the primary metallic tube;
- 5 closing the primary metallic tube;
- swaging and drawing the primary metallic tube to reduce its diameter;
- rolling the primary metallic tube to form a tape;
- twisting the tape into a generally helical shape; and
- applying sufficient heat to the primary metallic tube to sinter the
- 10 precursors, thereby to form a ceramic-composite superconducting tape with an inner superconducting ceramic filament and an outer metallic sheath.

Preferably, the method further includes the step, prior to the sintering step, of positioning one or more of the tapes within a secondary metallic tube, and drawing the secondary tube to reduce its diameter.

- 15 Preferably also, the tapes are positioned within the secondary tube prior to twisting the tape.

Preferably, the tapes are positioned within the secondary tube in one or more parallel stacks.

- More preferably, the twisting step includes the sub-step of twisting the
- 20 secondary tube after it has been drawn, thereby to impart the requisite twist to the tapes prior to sintering.



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Preferably, the twisting step is performed in a number of twisting sub-steps, at least some of the twisting sub-steps being separated by annealing steps.

5 Preferably, the drawing step is performed in a number of drawing sub-steps, at least some of the drawing sub-steps being separated by annealing steps.

Preferably, the degassing step includes the sub-step of placing the primary tube into a non-oxidising atmosphere. Preferably, the non-oxidising atmosphere is substantially nitrogen.

10 Preferably, the primary and/or secondary tubes are formed from silver or a silver alloy.

Preferably, the secondary tube includes a rectangular bore for receiving the tapes.

15 Preferably, the precursors packed into the primary tube includes Pb stabilised BSCCO-2223 ceramic material.

Substantial isotropy in the wire may be ascertained by placing a pair of voltage taps at a distance of  $D$  apart on the surface of the wire where  $D$  is greater than the pitch length of the twist about the longitudinal axis of the wire. Preferably,  $D$  is a whole number of the half twist pitches. In other  
20 embodiments,  $D$  is a whole number of twist pitches. A DC magnetic field of non zero magnitude is incident on the wire at an angle of 90 degrees to the longitudinal axis, and at an initial nominal angle of  $\alpha = 0$  degrees in the  $R-\phi$

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plane. The DC  $I_c$  is measured according to accepted practice. Magnetic isotropy is satisfied if equation 1 is met.

In a preferred embodiment, the anisotropic wires may be manufactured by stacking tapes, formed, for example, as described above, in parallel together, and placing the stack or stacks in a tube. The tube may then be drawn down. The anisotropic wire is then twisted such that overall the wire exhibits isotropic behaviour with respect to the effect of an applied magnetic field on  $I_c$ . The twisting may be performed in stages, advantageously with an annealing step between each stage. The tube may then be sintered and further drawn down prior to a subsequent heat treatment.

The incorporation of tapes of ceramic superconductors into a preferably round tube having a round bore may result in approximately 28% of the available cross-section of the tube bore being unfilled. In a preferred embodiment, the tube comprises a rectangular cross-section bore adapted to receive a multiplicity of layers of superconducting ceramic tape.

Suitable pitches required to achieve the desired degree of isotropy in the wire may be determined experimentally depending upon the application for which the wire is intended. For example, a transformer winding would desirably incorporate as short a twist as possible. In preferred embodiments, pitches of about 10mm may be obtained without resulting in a lowering of  $I_c$ . In applications where the wires are formed into a cable, pitches of about 14mm may be suitable.

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Ceramic superconductor materials for use in the present invention include, but are not limited to, ceramic high temperature superconductors such as Yttrium Barium Copper Oxide ( $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ ) (YBCO-123); Bismuth Strontium Calcium Copper Oxide ( $\text{BiSr}_2\text{Ca}_2\text{Cu}_1\text{O}_2$ )<sub>x</sub> (BSCCO-2212);

5 Thallium Barium Calcium Copper Oxide ( $\text{Tl}_1\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ) (TBCCO-1223); Thallium Barium Calcium Copper Oxide ( $\text{Tl}_2\text{Ba}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ ) (TBCCO-2212); Thallium Barium Calcium Copper Oxide ( $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ) (TBCCO-2223); Mercury Barium Calcium Copper Oxide ( $\text{Hg}_1\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ) (HBCCO-1223); and -1212 type superconductors such as  $[(\text{Pb},\text{Cd}).\text{Sr}_2(\text{Y},\text{Ca})\text{Cu}_2\text{O}_7]$ ; but

10 BSCCO-2223, Lead stabilised Bismuth Strontium Calcium Copper Oxide, is preferred.

Precursor materials of the ceramic superconductor materials include oxides, carbonates, nitrates and other compounds which contain the metal elements in the desired proportions. Where the precursor materials are a

15 mixture of separate components, the components are generally combined in amounts which promote the formation of the ceramic superconductor material. For example, in the formation of BSCCO-2223, the desired precursor materials are powders prepared by co-decomposition of metal nitrate solutions having the cation ratio of Bi:Pb:Sr:Ca:Cu = 1.84:0.35:1.91:2.05:3.06.

20 The powders may be calcined and may contain the -2212 as the major phase. The precalcined powders may be transformed to the -2223 phase by sintering at about 1103K.

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The ceramic superconductor material or precursor material thereof may be formed into a structure suitable for deformation by any convenient means, including by moulding, pressing, slip casting and extrusion.

The at least one ceramic superconducting tape may be formed by any  
5 convenient means. Such means include by the PIT technique, a Doctor/Blade process, a dip coating process and the like. Processes such as the PIT technique result in the ceramic superconductor material, or precursor material thereof being encased in a metal conductor. Processes such as the doctor/blade and the dip coating process result in the ceramic superconductor  
10 material or precursor material thereof forming a thick film on a metal substrate. It will be understood that the process by which the tape is formed is not narrowly critical. However, in preferred embodiments of the invention the formation of the elongate metal composite with a ceramic superconductor material or precursor material thereof by the PIT technique is particularly  
15 advantageous.

The metal selected to support the ceramic superconducting material is typically selected according to the desired properties of the tape. For example, in the production of high temperature superconducting wires or tapes, it is desirable to use silver or silver alloys to support the high  
20 temperature superconducting material in particular, while other metals and metal alloys may be identified, silver, dispersion strengthened silver, and dilute silver alloys such as with up to 4% gold for example 2% gold, have been found to be very effective. Other effective materials include silver-

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magnesium alloys, whereby the magnesium content is preferably less than 1%.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a cross-sectional micrograph of a 1X11 z-stack multifilamentary tape-in-tube according to the invention;

Figure 2 is a cross-sectional micrograph of a 2X11 multifilamentary tape-in-tube example according to the invention;

Figure 3 is a graph of  $I_c$  as a function of applied magnetic field for the example of Figure 2, and included for comparison,  $I_c$  behaviour with applied magnetic field directed along the a-b and c tape axes respectively of a conventional 27 multifilamentary flat tape;

Figure 4 is a graph of  $I_c$  as a function of applied magnetic field for the example of Figure 2 at 77K;

Figure 5 is a graph of  $I_c$  as a function of applied magnetic field for the example of Figure 2 at 4.2K;

Figure 6 is a micrograph of a restacked 2X7 multifilamentary tape-in-tube example according to the invention;

Figure 7 illustrates the experimental arrangement employed in characterising the example of Figure 6; and

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Figure 8 graphically illustrates  $I_c$  as a function of the resulting magnetic field performance of the twisted sample (curve 1) of Figure 6 and an untwisted sample (curve 2).

## PREFERRED EMBODIMENTS OF THE INVENTION

### 5 **EXAMPLE 1**

A charge of partially-reacted commercial (Bi, Pb)-2223 powder of nominal stoichiometry  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}\text{Ca}_{2.03}\text{Cu}_{3.06}\text{O}_{10.8}$  was packed into a silver (99.99%) tube (1mm wall) which had been crimp-sealed at one end. After the powder was fully loaded, the packing end was also closed.

10 After a de-gassing procedure, the packed tube was swaged and then subjected to a series of drawing passes, reducing its diameter, to form a ceramic-metal composite wire with an inner ceramic core and outer metallic sheath. All mechanical deformation in the experiment, including the drawing schedule consisted of reduction of approximately 15% per die pass. That is,  
15 the packed tube was drawn through a die a plurality of times, reducing its diameter approximately 15% per draw. After the final drawing reduction, the round composite wire was rolled into a flat tape 0.3mm thick.

Multifilamentary samples of tape-in-tube wires were fabricated by packing a plurality of the flat tapes into another round Ag tube (99.99%, wall  
20 thickness = 1mm), in the following manner, with control of the tape orientation inside the round tube ensuring that the tapes remained substantially parallel.

A particular re-stack tube was fabricated in one example by placing a stack of 11 tapes on top of each other and inserting the stack into the Ag

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tube, the tube having an inner diameter of 8mm and an outer diameter of 10mm. Another example was fabricated in by placing 2 parallel stacks of 11 tapes side by side into an identical tube. After stacking the 11 or 2 x 11 flat tapes into the second tube, the restacked tube was drawn to wire and heat treated. There was no rolling operation.

The twisting procedure for both examples was as follows. After drawing to a diameter of 1.54mm, the wire was twisted to a pitch of 10mm in the following steps: Pitch = 66,33,15mm, with intermediate annealing at 873K for 10 minutes in between each step. Twisting of short lengths was achieved by clamping the ends of the wire in vice grips, and counter rotating the ends a half turn to achieve one twist pitch in the wire. About 6 twist pitches were imparted to the wire between each annealing step.

Longer lengths of wire may be twisted by varying degrees at each later stage of reduction, with intermediate annealing between each draw pass. This may be achieved with a rotating die assembly.

After a first sinter, the wires of the examples were reduced further in diameter to 1.42mm without further twisting. This elongated the twist pitch by about 10%.

Finally the wires were sintered at  $1043\text{K} \leq T \leq 1113\text{K}$  for times up to 100 hours, in flowing synthetic air.

The current-voltage (I-V) characteristics of the wires at 77K, in self-field, were determined using a four-point technique with voltage contact spaced 70mm apart, using a voltage criterion of  $0.1\mu\text{Vmm}^{-1}$ . After each

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measurement, the current was reversed to prevent spurious results arising from localised heating. Isothermal transport critical current measurements were performed in applied DC fields up to  $7 \times 10^5 \text{ Am}^{-1}$  at 77K, with the sample able to be rotated  $\phi=360^\circ$  about the longitudinal axis of the wire, while  
 5 suspended between the poles of an electromagnet. In addition,  $I_c$  measurements at temperatures  $T=4.2 \text{ K}$  and 70K in applied fields up to  $8 \times 10^6 \text{ Am}^{-1}$  orientated along the wire in a first axial alignment and in a second perpendicular axial alignment were also carried out on the wires and compared with corresponding measurements on tape.

10 The critical current density was calculated from  $I_c/s$ , where  $s$  is the cross-sectional area in the ceramic core. A Kontron KS 300 image analysis software package connected to a Carl Zeiss optical microscope was used to obtain the area,  $s$ . The wire samples were analysed by employing back-scattered electron microscopy (SEM-BS) using a Jeol JSM 5400 LV electron  
 15 microscope. SEM samples (8 mm in length) were prepared by mounting in epoxy resin and mechanical polishing without any chemical etching.

Figure 1 shows a cross-sectional micrograph of the 1 x 11 z-stack multifilamentary tape-in-tube twisted wire of the example. This sample had a fill-factor of 18% and filament thickness of  $60 \pm 20 \mu\text{m}$ . At 77K, in self-field,  
 20 the sample shown in Figure 1 had an  $I_c=22 \pm 1 \text{ A}$ , corresponding to a  $J_c = 7.7 \times 10^7 \text{ Am}^{-2}$  ( $J_E=1.4 \times 10^7 \text{ Am}^{-2}$ ). Geometrical calculations show that the multi-tape structure of Figure 1 has a non-ideal initial packing fraction = 0.56. The packing fraction can be advantageously increased to 0.76 by using different



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cross sectional area tapes to re-stack. Such a wire is illustrated in Figure 2 which is a cross-sectional micrograph of the 22(2 x 11) multifilamentary tape-in-tube wire of the example. The sample in Figure 2 had a fill factor of 20%, and at 77K, in self-field, also had an  $I_c = 22 \pm 1$  A, corresponding to a  $J_c = 7 \times 10^7 \text{ Am}^{-2}$  (similarly with  $J_E = 1.4 \times 10^7 \text{ Am}^{-2}$ ). The packing fraction of approximately 0.80 for this tape compares favourably to that obtained from a conventional round wire re-stacking procedure which yields an initial packing fraction of 0.74.

Figure 3 shows a plot of the observed  $I_c$  versus applied field at 77K of the twisted round wire of the 2X11 multifilamentary tape-in-tube example, having a 14mm twist pitch. For comparison, the observed  $I_c$  behaviour with applied field along the a-b and c tape axis respectively is also shown for a conventional 27 multifilamentary flat-tape. The observed  $I_c$  overall dependence on an applied field for the round z-stack wire was in-between that of the a-b:c axial applied field anisotropy for the conventional multifilamentary powder-in-tube tape, showing that the 14mm twist pitch provides a degree of homogeneity of the field direction - dependence of these tapes. The results were also supported by magnetisation measurements.

Plotted data comparing  $I_c$  versus applied magnetic field ( $I_c$ -B), measured by the procedure described above, for the tape and round wire compared in Figure 3 shown in Figure 4 (77K) and Figure 5 (4.2K). The figure legends are as follows:

H//c     I-B for tape with field applied perpendicular to the tape surface;

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- H//ab I-B for tape with field applied parallel to tape surface;  
wire I-B for isotropic wire; and  
wire2 I-B for isotropic wire with field applied 90° from previous set.

- 5 It is to be noted that, at each temperature, the two data sets for the wire are virtually co-incident, indicating an overall isotropic I-B property for the wire.

### **EXAMPLE 2**

- A partially reacted commercial (Bi, Pb)-2223 powder of nominal  
10 stoichiometry  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}\text{Ca}_{2.03}\text{Cu}_{3.06}\text{O}_{10.8}$  was packed into a 99.99% silver tube having a 1mm wall thickness and crimp sealed at one end. After the powder was fully loaded, the packing end was closed. In other embodiments, however, the silver packing tube may include an inner cross-section being square or polygonal.
- 15 The loaded tube was degassed by heating to 923K for approximately 3 hours. The packed tube was then swaged and subjected to a series of die drawing passes, reducing its diameter, to form a ceramic-metal composite wire with an inner ceramic core and outer metallic sheath. All mechanical deformation in the process, including drawing, provided a reduction in  
20 diameter of approximately 15% per pass. After the final drawing reduction, the composite was drawn down to a diameter of 2.13mm.

The wire was rolled to a flat tape of thickness 0.80mm. This rolling was conducted in steps such that the completion of each step corresponded to a

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flat tape thickness of 2.13, 1.80, 1.50, 1.20, 1.00 and 0.80mm. No annealing of the wire occurred to this point.

A plurality of flat tapes were stacked in an array inside a round 99.99% silver tube having a wall thickness of 0.75mm. The flat rolled tape was  
5 divided into sections of approximately 100mm length and arranged in two parallel stacks of 7 tapes each. This arrangement was found to be most suitable to fit into a silver tube having an internal diameter of 8.50mm. However, in other embodiments of the invention, the number of parallel stacks having a plurality of tapes in each can be selected to suit a silver tube having  
10 an arbitrary internal diameter.

This composite structure, or "restack", was degassed by heating to 923K for approximately 3 hours. The degassing was executed in a vacuum whose pressure did not exceed  $1.33 \text{ Nm}^{-2}$ .

The restacked composite structure was then drawn down to a diameter  
15 of 1.54mm. This result is shown in Figure 6.

The annealing of the composite restacked structure during drawing was conducted in an inert atmosphere by flushing with nitrogen gas. The nitrogen gas advantageously prevented the magnesium alloy present in the packing tube from oxidising, and hence hardening, during the mechanical  
20 deformation stages.

The resulting drawn restacked composite structure, or wire, had three 150mm lengths divided from it. Each wire was subject to twisting about its longitudinal axis wherein each of the three wires respectively experienced 15,

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8 and 4 longitudinal turns over their lengths. The respective pitches of the twisted wires was 5, 10 and 20mm.

During the twisting procedure, annealing was carried out periodically to relieve the work hardening and deterioration of the filament structure. The annealing during this process was carried out in an oven having an inert atmosphere of nitrogen at 773K for three minutes. The annealing was effected after every two 360° twists of each end of the respective wires. In other embodiments, annealing is effected after each 360° twist of the wire. That is, the annealing was effected for ends of the wire being rotated 360° with respect to each other.

In addition to the three 150mm sample lengths used in the twisting process, an untwisted control sample of 200mm length was also selected. The control sample was drawn down to a diameter of 1.54mm, the same as the three 150mm lengths. Both the three 150mm sample lengths and the control sample were sintered in identical fashions during the drawing process. Upon completion of the first sinter for each of the wires, their diameters by drawing were further reduced to 1.45mm. This represented a reduction in cross-sectional area of 14% and a reduction in diameter of 6%. Each of the samples were then subjected to a second sinter as previously detailed.

Figure 6 presents a representative example of the cross-section of one of the three 150mm samples. The diameter of the wire illustrated in figure 6 is 1.45mm.

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An arbitrary one of these twisted 150mm wires and the control wire were characterised by employing the following technique. A sample of twisted wire was cooled to 77K in a magnetic field of fixed magnitude of 4.05mT and directed perpendicular to the longitudinal axis of the wire. Voltage contacts in the wire structure, used to measure the critical current of the sample, were placed an integral number of twist pitches apart. In this embodiment, the sample having a pitch of 5mm corresponding to 15 turns along its 150mm length, was chosen. Distance between these voltage contacts was arbitrarily chosen to be 10mm. Repeated measurements suggested voltage contacts were spaced a distance of  $11 \pm 0.5\text{mm}$  as a result of practicalities in soldering the contacts.

Having an initially randomly oriented magnetic field perpendicular to the longitudinal axis of strength 4.05mT, the critical current was found to be 5.5A. Figure 7 schematically depicts the arrangement of the magnetic field.

Figure 8 graphically illustrates the resulting magnetic field performance of the twisted sample (curve 1) and the untwisted sample, or control wire (curve 2), when the magnetic field direction was swept in an arc of  $180^\circ$  of  $5^\circ$  steps at a constant magnitude. The magnetic field was constantly directed normal to the longitudinal axis of the wire, and the critical current after each  $5^\circ$  was measured. As is apparent from Figure 8, the critical current density for the twisted wire varied by less than 5% of the initial critical current for each  $5^\circ$  rotation of the magnetic field.

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Curve 2 of the figure denotes the results for the 200mm control sample of untwisted wire subjected to the same test. Results of the normalised critical current shows a variation of more than 30% from the initial critical current for the initial critical current for the untwisted wire. It is apparent, therefore, that a clear advantageous result is achieved by twisting the wire about its longitudinal axis.

These results suggest that the tape-in-tube technique may provide a suitable route to manufacture practical circular wire superconductors. From an engineering point-of-view, optimum tape-in-tube round wires should have as homogenous a transverse  $J_c$  dependence as possible, and be manufactured to tight confirmation tolerances. This is because, unlike the high a-b:c aspect ratio tapes, round wires will have no physically discernible external features to characterise their anisotropy. However, the superconducting filamentary structure within the wires will still be anisotropic and so the best  $I_c$  will still be obtained if the filaments contain well-textured, aligned grains.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit and scope. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or

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features. Although the invention has been described with reference to particular examples, it will be appreciated by those skilled in the art that it may be embodied in many other forms.

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## CLAIMS:-

1. An axially extending wire including a substantially axially extending superconducting filament which is flattened in cross section, the superconducting filament being twisted along at least a substantial portion of its length into a substantially helical shape, such that the wire is:
  - substantially anisotropic in relation to the effect of an applied magnetic field on the critical current  $I_c$  at any cross-sectional point along the wire's length; and
  - substantially isotropic in relation to the effect of an applied magnetic field on the critical current  $I_c$  along a substantial length of the wire.
2. An axially extending wire according to claim 1, wherein the filament is rotationally asymmetrical about the axis at each point along the length of the wire.
3. An axially extending wire according to claim 1 or 2, wherein the anisotropic and isotropic conditions are satisfied in relation to a magnetic field applied in a plane substantially normal to the axis.
4. An axially extending wire according to any one of the preceding claims, including a plurality of the filaments arranged, in cross section, in at least two parallel stacks.
5. An axially extending wire according to claim 4, wherein each stack contains a plurality of the filaments.
6. An axially extending wire according to any one of the preceding claims, wherein the filaments are embedded in a silver or silver alloy matrix.



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7. An axially extending wire according to any one of the preceding claims, wherein a pitch of the helical shape is selected on the basis of an application to which the wire is to be applied.
8. An axially extending wire according to claim 7, wherein the pitch of the helical shape is selected on the basis of an expected minimum radius of curvature which the application to which the wire is to be applied.
9. An axially extending wire according to any one of the preceding claims, wherein the filaments include Pb stabilised BSCCO-2223 ceramic.
10. A method of fabricating a superconducting wire, the method including the steps of:
- providing a primary metallic tube;
  - packing precursors of ceramic high temperature superconducting material into the primary metallic tube;
  - applying heat to degas the contents of the primary metallic tube;
  - 15 closing the primary metallic tube;
  - swaging and drawing the primary metallic tube to reduce its diameter;
  - rolling the primary metallic tube to form a tape;
  - twisting the tape into a generally helical shape; and
  - applying sufficient heat to the primary metallic tube to sinter the
- 20 precursors, thereby to form a ceramic-composite superconducting tape with an inner superconducting ceramic filament and an outer metallic sheath.
11. A method of fabricating a superconducting wire according to claim 10, further including the step, prior to the sintering step, of positioning one or

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more of the tapes within a secondary metallic tube, and drawing the secondary tube to reduce its diameter.

12. A method of fabricating a superconducting wire according to claim 11, wherein the tapes are positioned within the secondary tube prior to twisting the tape.
13. A method of fabricating a superconducting wire according to claim 11, wherein the tapes are positioned within the secondary tube in one or more parallel stacks.
14. A method according to claim 12 or 13, wherein the twisting step includes the sub-step of twisting the secondary tube after it has been drawn, thereby to impart the requisite twist to the tapes prior to sintering.
15. A method according to any one of claims 10 to 14, wherein the twisting step is performed in a number of twisting sub-steps, at least some of the twisting sub-steps being separated by annealing steps.
16. A method according to any one of claims 10 to 15, wherein the drawing step is performed in a number of drawing sub-steps, at least some of the drawing sub-steps being separated by annealing steps.
17. A method according to any one of claims 10 to 16, wherein the degassing step includes the sub-step of placing the primary tube into a non-oxidising atmosphere.
18. A method according to any one of claims 10 to 17, wherein the non-oxidising atmosphere is substantially nitrogen.

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19. A method according to any one of claims 10 to 18, wherein the primary and/or secondary tubes are formed from silver or a silver alloy.
20. A method according to any one of claims 10 to 19, wherein the secondary tube includes a rectangular bore for receiving the tapes.
- 5 21. A method according to any one of the preceding claims, wherein the precursors packed into the primary tube includes Pb stabilised BSCCO-2223 ceramic material.
22. A superconducting wire manufactured in accordance with the method of any one of claims 10 to 22.

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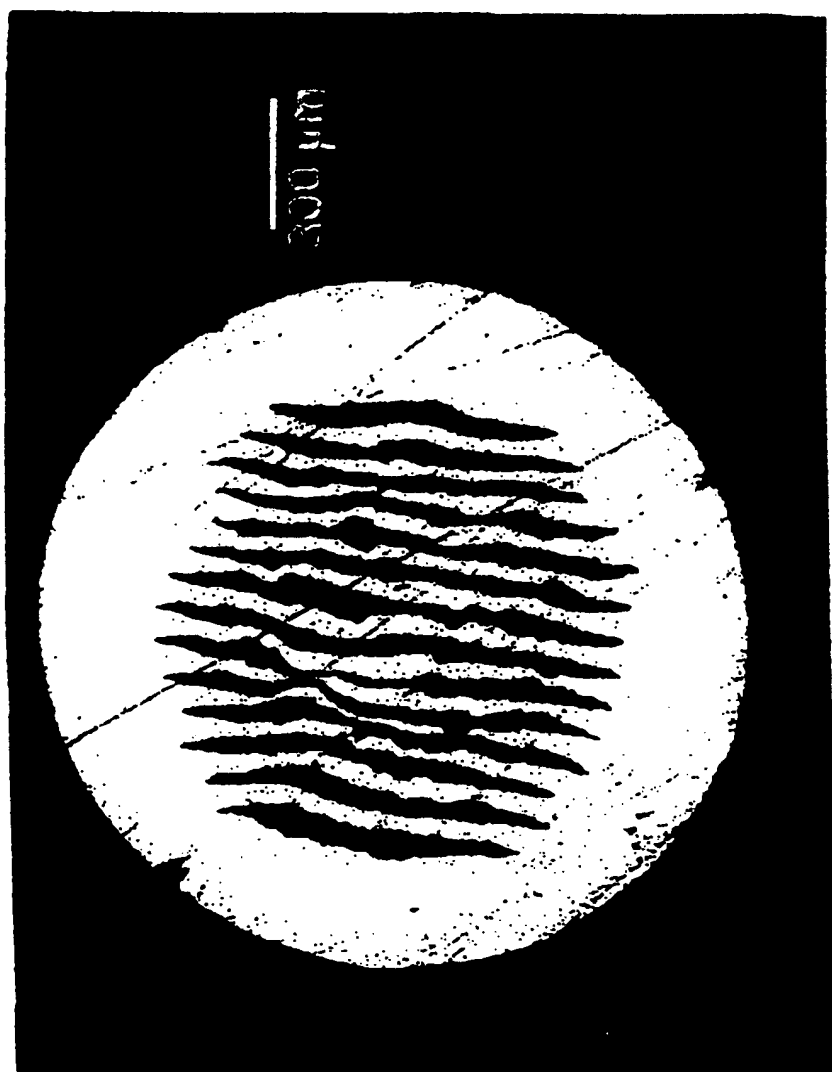


FIGURE 1

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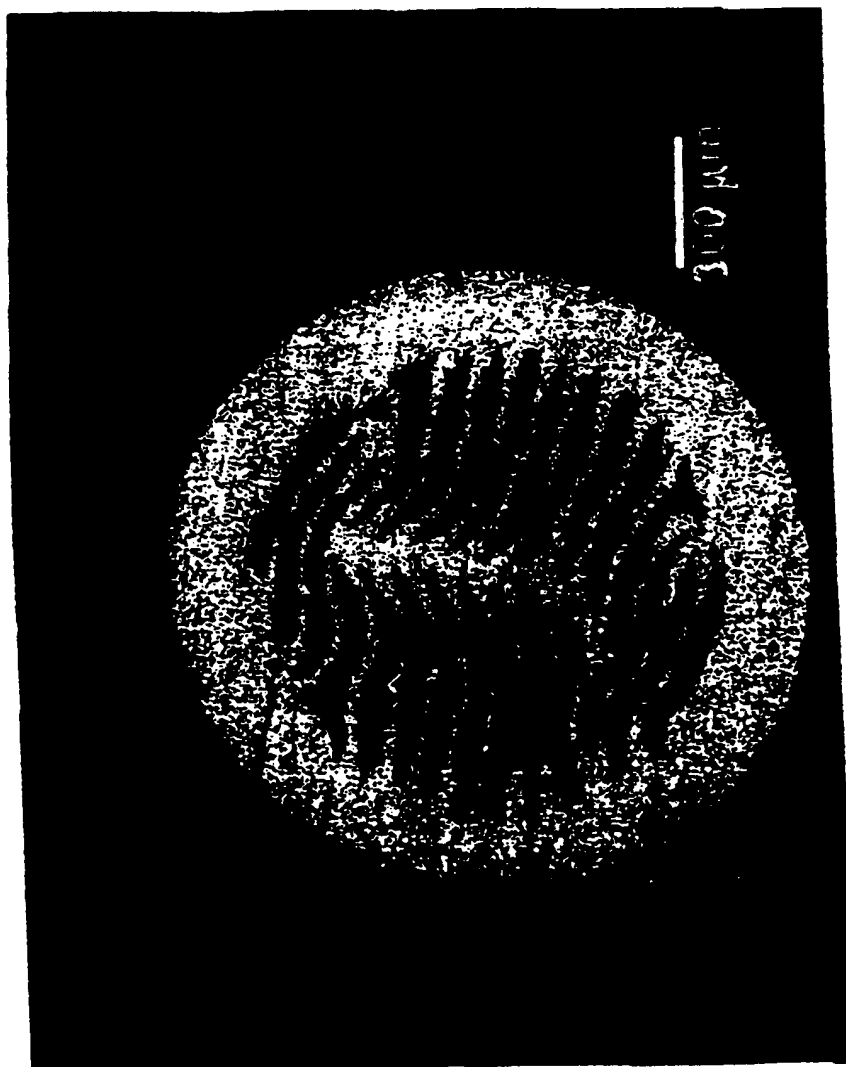


FIGURE 2

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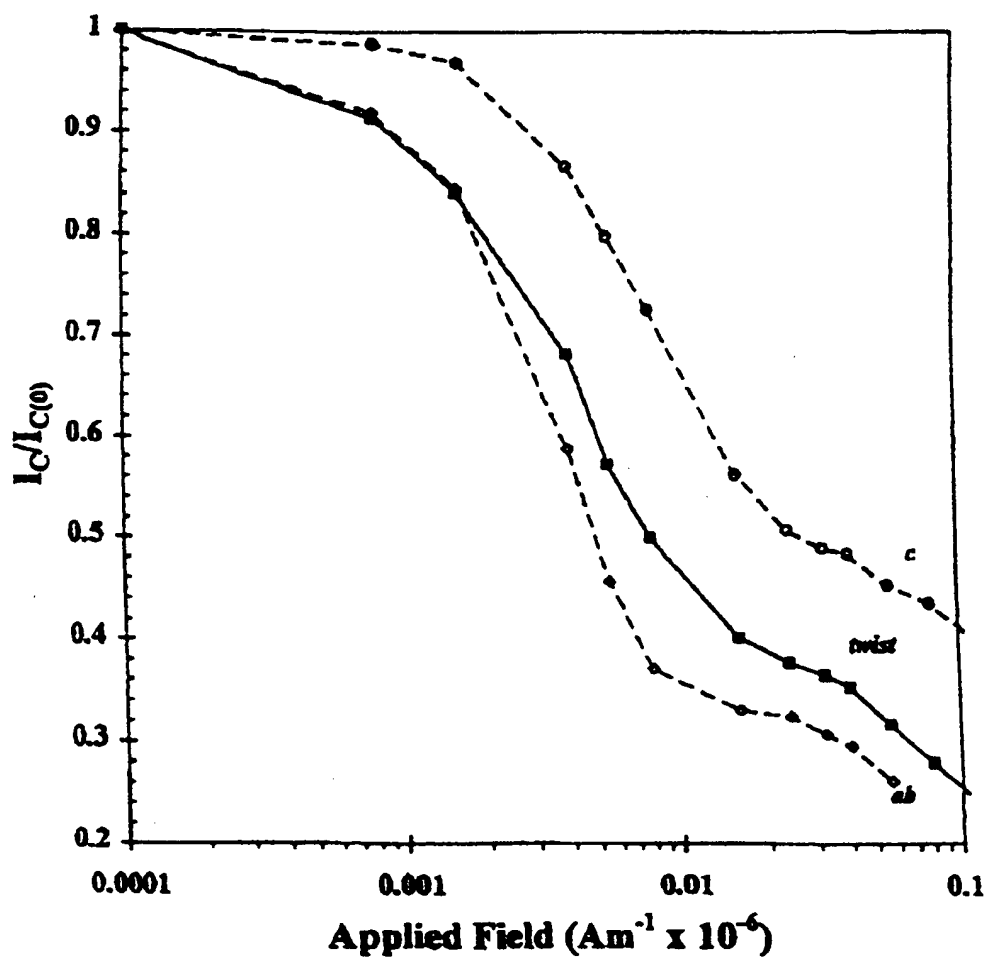
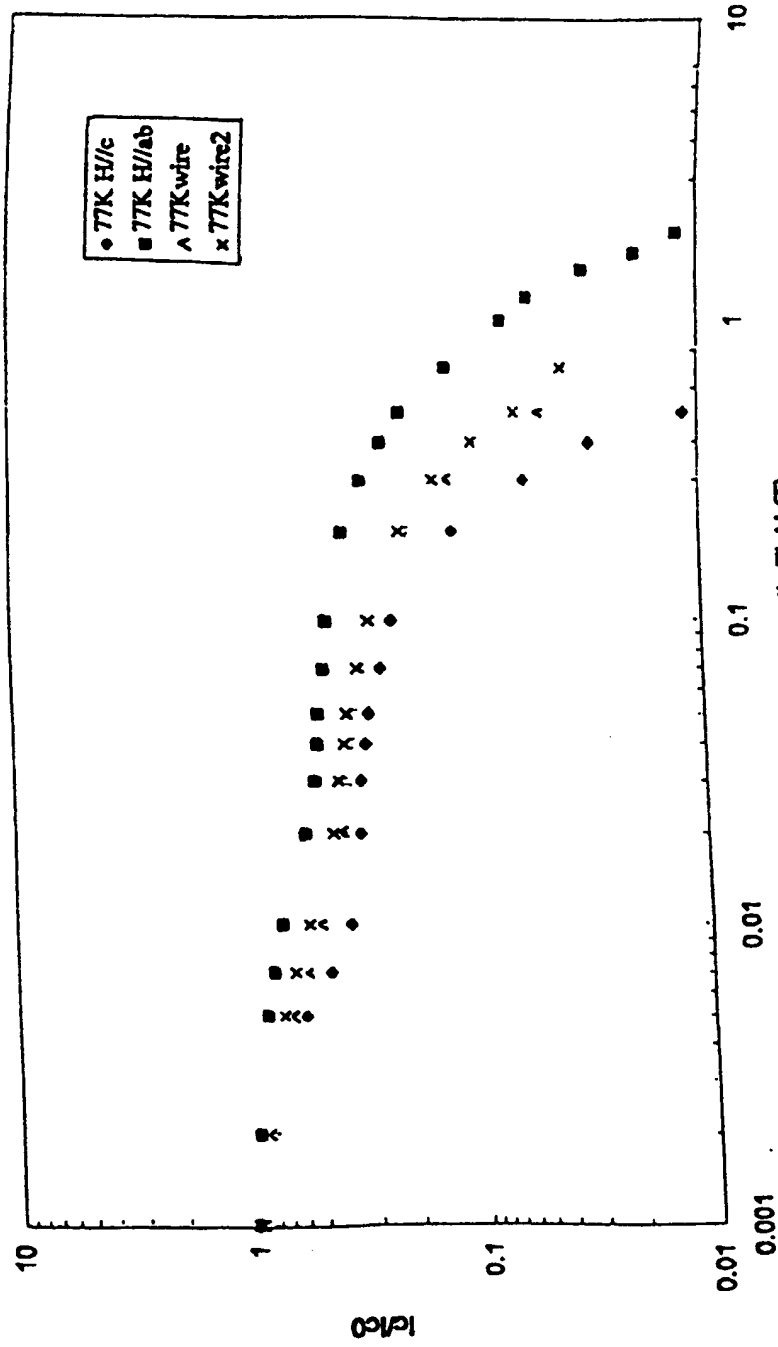


FIGURE 3

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Field Performance of HTS Tape and Wire



Applied Magnetic Field (T)

FIGURE 4

Field Performance of HTS Tape and Wire at 4.2K

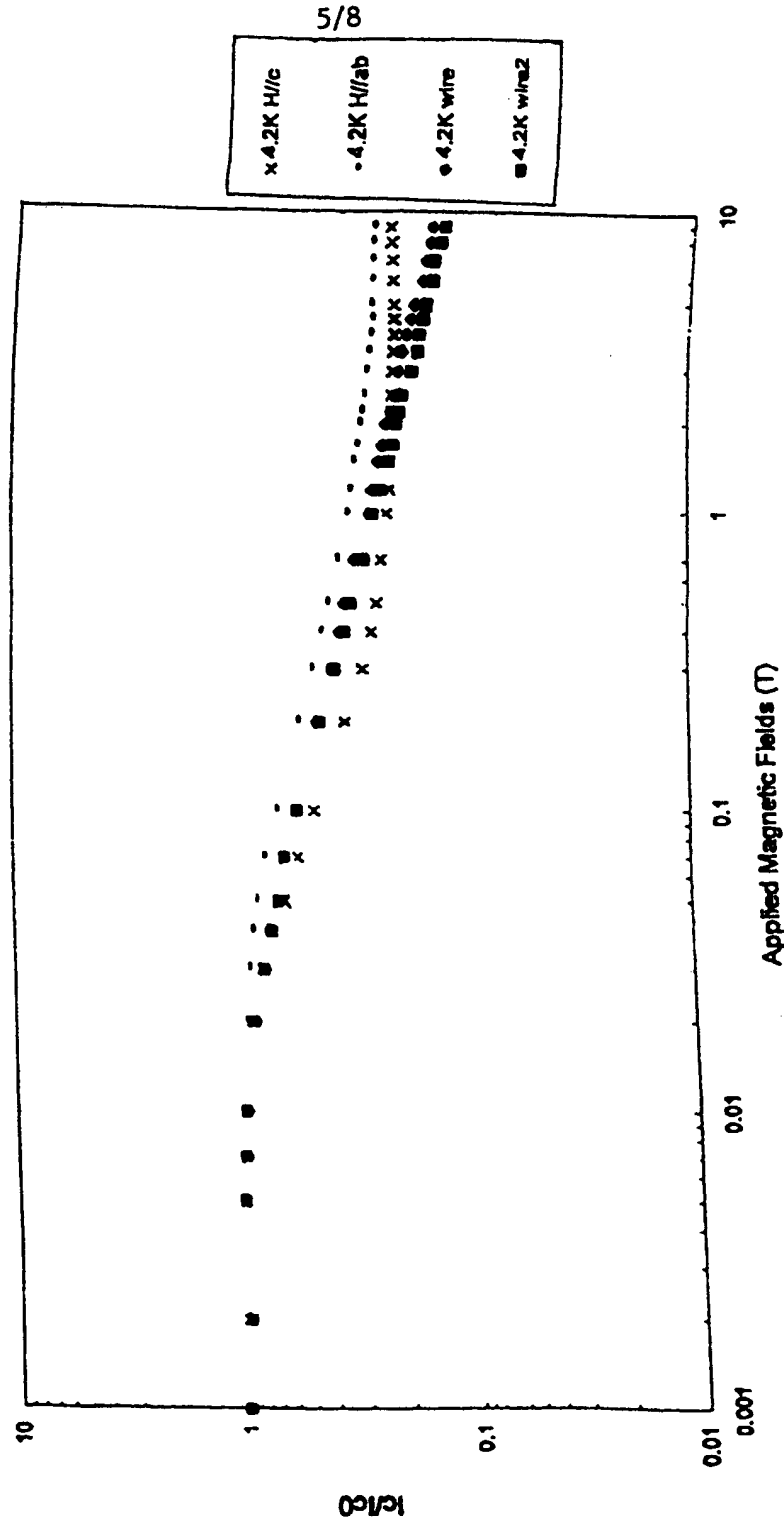


FIGURE 5



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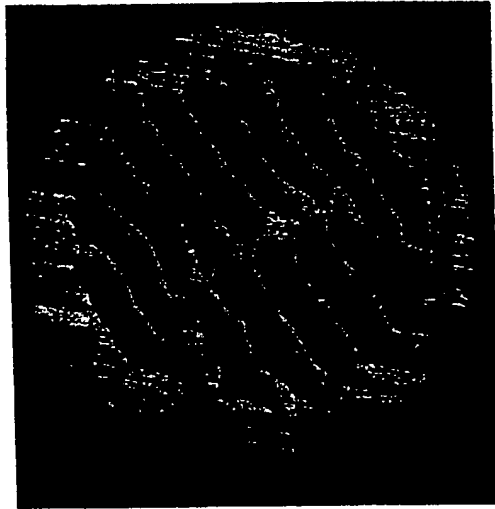
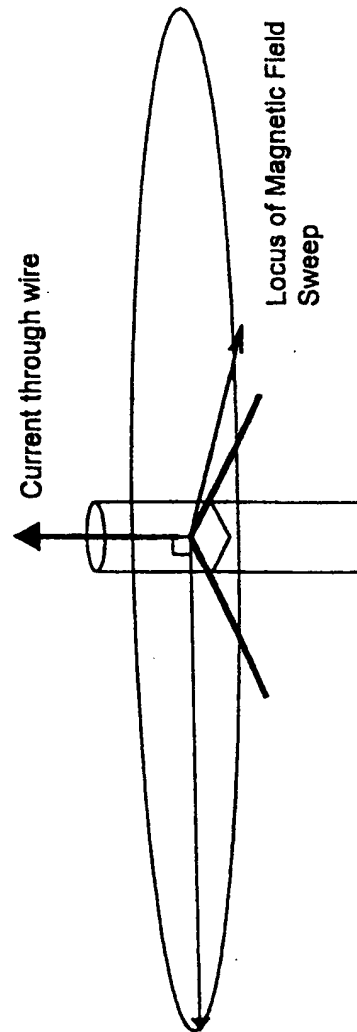
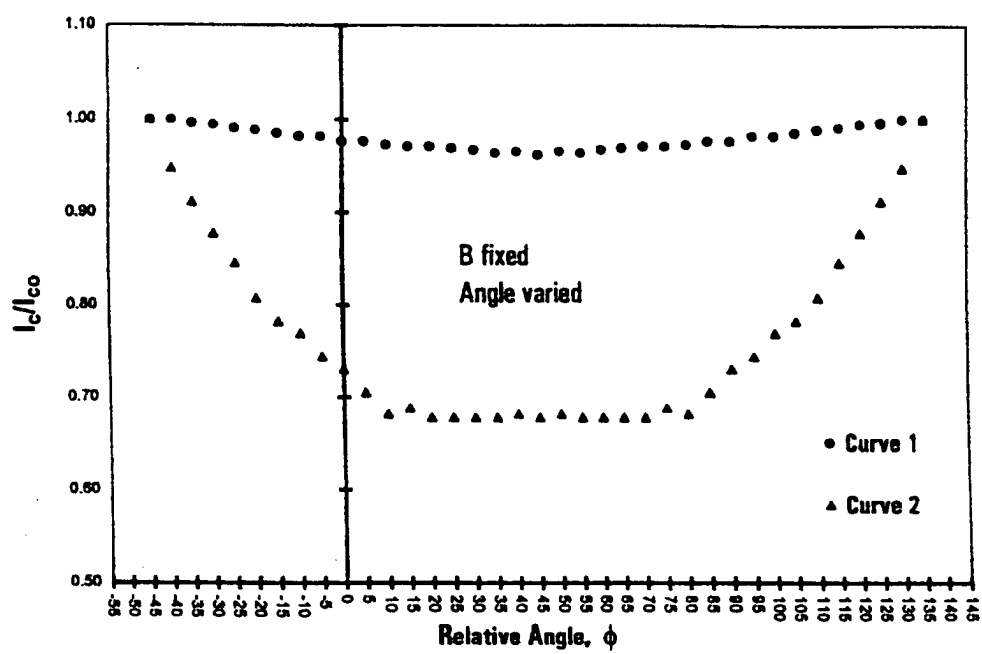


Figure 6



**Figure 7**

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Figure 8

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 99/00527

**A. CLASSIFICATION OF SUBJECT MATTER**Int Cl<sup>6</sup>: H01B 12/08, 12/10, 13/00, H01L 39/24

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC: H01B, H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPAT, JAPIO, INSPEC

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5706571 A (DUPERRAY et al) 13 January 1998 Whole document	1-22
X	EP 503525 A (ABB PATENT GmbH) 16 September 1992 Figure 1	1-22
X	EP 638942 A (SUMITOMO ELECTRIC INDUSTRIES, LTD) 15 February 1995 Figures 1-4	1-22

☒ Further documents are listed in the continuation of Box C☒ See patent family annex

* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
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Date of the actual completion of the international search  
26 July 1999Date of mailing of the international search report  
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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 99/00527

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 736914 A (SUMITOMO ELECTRIC INDUSTRIES, LTD) 9 October 1996 Whole document	1-22
X	WO 96/08045 A (AMERICAN SUPERCONDUCTOR CORPORATION) 14 March 1996 Figures 1, 2	1-22
X	WO 97/17706 A (AMERICAN SUPERCONDUCTOR CORPORATION) 15 May 1997 Whole document	1-22
X	JP 4-155711 A (CENTRAL RESEARCH INST OF ELECTRICAL POWER IND) 28 May 1992 Figures	1-22

# INTERNATIONAL SEARCH REPORT

## Information on patent family members

International application No.

PCT/AU 99/00527

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	5706571	CA	2185578	EP	763860	FR	2738948
		JP	9129052				
EP	503525	DE	4108445	JP	5078991		
EP	638942	JP	7105753				
EP	763914	JP	8335414				
WO	9608045	AU	35842/95	CA	2198098	EP	780024
		JP	10512387	NZ	293410		
WO	9717706	AU	11165/97	EP	860012		
							END OF ANNEX